

PATENT ABSTRACTS OF JAPAN

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(54) ADHESIVE RESIN PARTICLE FOR SPACER OF LIQUID CRYSTAL ELEMENT AND SPACER COMPOSITION OF LIQUID CRYSTAL ELEMENT

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a liquid crystal element of stable characteristics which surely adheres two opposite substrates to each other and prevents the unequal presence of spacers.

SOLUTION: The resin particles consist of (meth)acrylic adhesive resin particles formed by copolymerization of 10 to 60 pts.wt. glycidyl (meth)acrylate and/or 1 to 10 pts.wt. alkoxysilane compd. with a (meth)acrylic adhesive resin. The spacer compsn. consists of the spacers and 10 to 10000 pts.wt. adhesive resin particles per 100 pts.wt. spacer component.

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CLAIMS

[Claim(s)]

[Claim 1] (Meta) The adhesive resin particle for the spacers of a liquid crystal device which becomes acrylic adhesive property resin from the acrylic (meta) adhesive property resin particle which glycidyl (meta) acrylate 10 – 60 weight sections, and/or the alkoxysilane compound 0.1 – 10 weight sections copolymerized.

[Claim 2] The adhesive resin particle for the spacers of the liquid crystal device according to claim 1 characterized by being in within the limits whose mean particle diameter of the aforementioned (meta) acrylic adhesive property resin particle is 1–20 micrometers.

[Claim 3] The adhesive resin particle for the spacers of the liquid crystal device according to claim 1 characterized by the glass transition temperature of the aforementioned (meta) acrylic adhesive property resin particle being 20 degrees C or more.

[Claim 4] The spacer constituent of the liquid crystal device characterized by being the spacer constituent of a liquid crystal device which consists of an adhesive resin particle of the 10 – 10000 weight section to a spacer and this spacer component 100 weight section, and this adhesive resin particle being an acrylic (meta) adhesive property resin particle which glycidyl (meta) acrylate 10 – 60 weight sections, and/or the alkoxysilane compound 0.1 – 10 weight sections copolymerized to acrylic (meta) adhesive property resin.

[Claim 5] The spacer constituent of the liquid crystal device according to claim 4 characterized by being in 101 – 200% of within the limits to the distance between substrates of the liquid crystal device to which it is in within the limits whose distance between substrates of the liquid crystal device secured by said spacer is 1–10 micrometers, and (meta) the mean particle diameter of an acrylic adhesive property resin particle is secured by this spacer.

[Claim 6] The spacer constituent of the liquid crystal device according to claim 4 characterized by the glass transition temperature of the aforementioned (meta) acrylic adhesive property resin particle being 20 degrees C or more.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001] [Industrial Application] This invention relates to the spacer constituent containing the adhesive resin particle which carries out adhesion immobilization of the substrate which is blended with a spacer in a liquid crystal device, and confronts each other, and this adhesive resin particle. While forming the gap which can be filled up with liquid crystal furthermore between the substrates which carry out heating sticking by pressure of the substrate which this invention does not have a possibility of polluting liquid crystal, and confronts each other, and stand face to face against a detail, the fall of the display function of the liquid crystal by such adhesion component is related with the spacer constituent of a few and suitable adhesive resin particle to manufacture especially a large-sized liquid crystal device and this adhesive resin particle liquid crystal device.

[0002]

[Description of the Prior Art] The liquid crystal device which poured liquid crystal into the gap which confronted the plate-like electrode substrate of a pair in parallel is known.
[0003] Conventionally, in order to hold uniformly the gap of the substrate for being filled up with liquid crystal, the spacer particle is used for such a liquid crystal device. Since the silica particle or the divinylbenzene resin particle is used as a liquid crystal device using such a spacer particle and such a spacer particle does not have the adhesive property to the substrate, in case such a spacer particle manufactures a liquid crystal device, it may move in the inside of the gap where it filled up with liquid crystal on the occasion of actuation of the liquid crystal device of impressing an electrical potential difference to a liquid crystal device etc. Although it is hard to become so big a problem even if a spacer particle is unevenly distributed to some extent when the area of a liquid crystal display part is small, the fall of the liquid crystallinity ability by the maldistribution of such a spacer particle has been a problem with enlargement of a liquid crystal display screen recently.

[0004] Pasting up mutually the substrate which blends an adhesive resin particle with a spacer and confronts each other by the adhesive resin particle under such a situation is proposed. For example, the powdered glue which blended the spacer particle and the spherical polymer particle with JP.62-258426A so that the spacer particle whose friction withstand voltage to iron powder is AmuC/g , and the adhesion particle whose friction withstand voltage is BmuC/g might have the relation of the following specification is indicated.

[0005]

$$\left| \frac{A}{B} - 1 \right| \leq 30 \mu\text{C/g}$$

[Equation 1]

[0006] This invention tends to make a spacer particle stick to the perimeter of a polymer particle in static electricity, and tends to prevent the maldistribution of a spacer particle.
[0007] Moreover, an epoxy system adhesive property resin particle, a polyolefine system resin particle, an ionomer resin particle, a polyester system resin particle, an acrylic resin particle, etc. are used as an adhesive resin particle used for such a liquid crystal device. However, into such a

resin particle, the liquid crystal compound with which it fills up with the additive of the low molecular weight of a curing agent etc. may receive a bad influence.
[0008] For example, spherical particle adhesives with which a principal component becomes JP.3-47877A from an epoxy resin at least and particle diameter of 0.3-500 micrometers which comes to carry out partial hardening with a water-soluble curing agent inside this spherical particle, including a potential mold-curing agent Epoxy system particle-like adhesives are indicated. While such an adhesive resin particle has the good adhesive property to the substrate which confronts each other, after pasting up a substrate, it is desirable to form an immobilization object so that a bad influence may not be done to liquid crystal.

[0009] However, when using a resin particle which is indicated by the above-mentioned official report, for example, especially an epoxy resin, since the potential curing agent is blended with the interior of spherical particle adhesives, it may remain, without some potential curing agents reacting in the case of hardening. It may react with the liquid crystal compound with which such a residual curing agent had high reactivity, and it filled up, and the property of a liquid crystal compound may change with such reactions.

[0010] Thus, the adhesives used for a liquid crystal device need to be that in which the reactant radical does not remain, before filling up with a liquid crystal compound, and the conventional adhesives do not have the chemical stability enough [adhesives] to such a liquid crystal compound.

[0011] Moreover, the method of giving an adhesive property to the spacer itself [other than the approach different from a spacer particle as mentioned above using an adhesives particle as a particle] and preventing migration of a spacer particle is learned. For example, the enveloping layer which consists of a resin constituent containing a vinyl system polymer and a polyvalent-carboxylic-acid compound is formed in the front face of a core particle at JP.6-172659A, and pasting up a substrate by this enveloping layer is indicated.

[0012] Thus, although this spacer particle is pasted up to a substrate by forming an enveloping layer, the spacer particle in which the core of this spacer particle is formed in with the organic material or the inorganic material, therefore this enveloping layer was formed does not have the elasticity which may deform particle shape in the case of heating sticking by pressure. Therefore, adhesion arrival of such a spacer particle and a substrate is carried out, and they have the problem that the adhesion stability of the spacer particle to a substrate is inadequate.
[0013]

[Problem(s) to be Solved by the Invention] Since this invention is made in view of the trouble of the conventional technique which was described above, does not contain a curing agent and is [it does not have a possibility that the display function of liquid crystal may fall and] excellent in the adhesive strength of a substrate, it aims at offering the spacer constituent of the adhesive resin particle for the spacers of a liquid crystal device which can be especially used for a large-sized liquid crystal device, and a liquid crystal device.
[0014]

[Summary of the Invention] This invention is in the adhesive resin particle for the spacers of a liquid crystal device which becomes acrylic (meta) adhesive property resin from the acrylic (meta) adhesive property resin particle which glycidyl (meta) acrylate 10 - 60 weight sections, and/or the alkoxysilane compound 0.1 - 10 weight sections copolymerized.

[0015] Moreover, the spacer constituent of the liquid crystal device of this invention is a spacer constituent of a liquid crystal device which consists of an adhesive resin particle of the 10 - 10000 weight section to a spacer and this spacer component 100 weight section, and it is characterized by this adhesive resin particle being an acrylic (meta) adhesive property resin particle which glycidyl (meta) acrylate 10 - 60 weight sections, and/or the alkoxysilane compound 0.1 - 10 weight sections copolymerized to acrylic (meta) adhesive property resin.
[0016] It is desirable that it is in 101 - 200% of within the limits to the distance between substrates of the liquid crystal device to which it is in within the limits whose distance between substrates of the liquid crystal device secured by said spacer is 1-10 micrometers, and (meta) the mean particle diameter of an acrylic adhesive property resin particle is secured by this spacer, and, as for the glass transition temperature of the aforementioned (meta) acrylic

adhesive property resin, it is still more desirable that it is 20 degrees C or more.

[0017] Such an adhesive resin particle has heating cross-linking, shows the field which contacts liquid crystal in a liquid crystal device, the orientation film usually formed from polyimide, and a very good adhesive property, and, moreover, does not do a bad influence to the liquid crystal formed in this way by most polymers serving as huge gel according to bridge formation between polymers by heating crosslinking reaction. Furthermore, this adhesive resin particle has elasticity, and it carries out heating bridge formation, being crushed by carrying out heating sticking by pressure. Therefore, an adhesive property with the orientation film and an adhesive resin particle good not adhesion arrival but in order to carry out face bonding does not change with time, and is maintained for a long period of time.

[0018]

[Detailed Description of the Invention] Hereafter, the spacer constituent of the adhesive resin particle for spacers of the liquid crystal device concerning this invention and a liquid crystal device is explained in order.

[0019] The adhesive resin particle for spacers of the liquid crystal device concerning this invention becomes acrylic (meta) adhesive property resin from the acrylic (meta) adhesive property resin particle which glycidyl (meta) acrylate 10 - 60 weight sections, and/or the alkoxyisilane compound 0.1 - 10 weight sections copolymerized.

[0020] The following acrylic adhesive resin is used for the adhesive resin particle for spacers of the liquid crystal device concerning such this invention. The resin obtained by carrying out the polymerization (**) of the acrylic compound generally expressed with the following type (A) type (meta) as acrylic adhesive property resin used by this invention (meta) is used.

[0021] $\text{CH}_2=\text{C}(\text{RCOOR}') \dots (\text{A})$

However, R is hydrogen or a methyl group among the above-mentioned formula (A), and R' is the radical of the monovalence which does not contain hydrogen.

[0022] As such (meta) an acrylic compound More specifically Methyl (meta) acrylate, ethyl (meta) acrylate, Propyl (meta) acrylate, butyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, Lauryl (meta) acrylate, stearyl (meta) acrylate, Cyclohexyl (meta) acrylate, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, chloro-2-hydroxyethyl (meta) acrylate, Diethylene-glycol monochrome (meta) acrylate, methoxy ethyl (meta) acrylate, Dicyclopentani(metha) acrylate, JISHIKURO pentenyl (meta) acrylate, isoboronyl (meta) acrylate, etc. (meta) An acrylic compound can be mentioned.

[0023] Although the polymer (**) using at least one sort of the above (meta) acrylic compounds as acrylic adhesive property resin used by this invention (meta) is used, you may be the copolymer of the kind and the following compounds of such an above-mentioned (meta) acrylic compound at least.

[0024] As an example of this (meta) acrylic compound and a copolymerizable compound, a styrene system compound, a vinyl system compound, and the compound of two or more organic functions can be mentioned. As an example of a styrene system compound, styrene system compounds, such as alkyl styrene, FUORO styrene, such as styrene, methyl styrene, dimethyl styrene, trimethyl styrene, propyl styrene, butyl styrene, hexyl styrene, heptyl styrene, and octyl styrene, chloro styrene, bromostyrene, dibromo styrene, iodation styrene; nitro styrene, acetyl styrene, and methoxy styrene, can be mentioned here.

[0025] Moreover, as an example of a vinyl system compound, halogenation vinylidenes, such as a conjugated diene compound; vinyl chloride, vinyl bromide, etc., such as vinylpyridine, vinyl pyrrolidone, vinylcarbazole, vinyl acetate and an acrylonitrile; butadiene, an isoprene, and a chloroprene, can be mentioned.

[0026] As an example of the compound of two or more organic functions, furthermore, ethylene glycol di(metha)acrylate, Diethylene GURIKORUJI (meta) acrylate, triethylene glycol di(metha) acrylate, Tetraethylene glycol di(metha)acrylate, TORIMECHI roll pro pantry (meta) acrylate, Pen TAERISURITORUORI (meta) acrylate, 1 and 1, and 1-trihydroxy methyl METANTORI acrylate, 1, 1, and 1-trihydroxy methyl ETANTORI acrylate, 1 and 1, and 1-trihydroxy MECHIRUPURO pantry acrylate, a divinylbenzene, and trivinylbenzene can be mentioned.

[0027] In the range which furthermore does not spoil the property of the adhesive resin particle

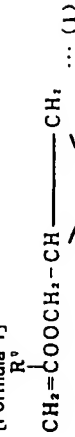
of this invention, addition polymerization nature partial saturation aliphatic carboxylic acid, such as a methyl (meta) acrylic acid, alpha-ethyl (meta) acrylic acid, a crotonic acid, alpha-methyl crotonic acid, alpha-ethyl crotonic acid, isocrotonic acid, tiglic acid and a UNGERIKA acid; maleic acid, a fumaric acid, an itaconic acid, a citraconic acid, mesaconic acid, glutaconic acid, and hydronalium muconic acid, etc. may copolymerize.

[0028] The adhesive resin particle for the spacers of the liquid crystal device concerning this invention consists of an methacrylic system resin particle which the alkoxyisilane compound shown in acrylic adhesive property resin (meta) which was described above at glycidyl (meta) acrylate and/or the following copolymerized.

[0029] The glycidyl (meta) acrylate used here is a compound shown below.

[0030]

[Formula 1]



[0031] However, in the above-mentioned formula (1), R0 is a hydrogen atom or a methyl group. In this invention, glycidyl methacrylate is especially desirable.

[0032] In addition, by this invention, epoxy compounds, such as glycidoxymethyl (meta) acrylate and glycidoxymethyl (meta) acrylate, can be used with glycidyl methacrylate within limits to which the adhesive property of an adhesive resin particle is not changed.

[0033] Furthermore -- this invention -- the above-mentioned glycidyl (meta) acrylate -- or the alkoxyisilane shown below instead of glycidyl (meta) acrylate can be used.

[0034] As an alkoxyisilane compound used by this invention, the silane compound expressed with the following type (2) and (3) types is used.

SIR1k R2m R34-k-m ... (2)

However, in the above-mentioned formula (2), k is 1-3, and it is m. Those with 0-2 and k+m are 1-3.

[0035] Moreover, R1 is a vinyl content radical and R2 is a univalent radical chosen from an alkyl group, an aryl group, an epoxy content radical, an amine content radical, a halogen radical, and an isocyanuric radical.

[0036] And when k is 2 or 3, you may differ, even if R1 is the same, and R3 is alkoxy groups, such as an alkoxy radical, an alkenyloxy radical, or an aryloxy group.

[0037] As the example of R1 -- a vinyl group -- and (meta) An acrylic content radical can be mentioned. Here, as an example of an acrylic (meta) content radical, an acrylate (meta) radical, an acryloxyethyl (meta) radical, an acryloxypropyl (meta) radical, an acryloxy (meta) methoxy propyl group, an acryloxy (meta) ethoxy propyl group, an acryloxy (meta) propoxy propyl group, etc. can be mentioned.

[0038] As an example of R2, a hydrogen atom, the alkyl group of carbon numbers 1-20, an aryl group, an epoxy group, an amine content radical, a halogen atom, and an isocyanuric radical can be mentioned.

[0039] Here, as an example of the alkyl group of carbon numbers 1-20, a methyl group, an ethyl group, a propyl group, butyl, etc. can be mentioned. As an example of an aryl group, the phenyl group which may have the substituent, the phenoxy group which may have the substituent can be mentioned.

[0040] As an example of an epoxy group, a glycidyl group, a glycidyl (meta) acrylate radical, a glycidyl ethyl group, a glycidyl propyl group, etc. can be mentioned. As an example of an amine content radical, an aminomethyl radical, an aminoethyl radical, an aminopropyl radical, an aminomethyl aminopropyl radical, an aminoethyl aminopropyl radical, etc. can be mentioned. [0041] And F, Cl, Br, I, etc. can be mentioned as an example of a halogen atom. In a formula (2), the alkoxy radical which has the hydrocarbon group of carbon numbers 1-20, the alkenyloxy radical which has the hydrocarbon group of carbon numbers 1-20, and an aryloxy group can be mentioned as an example of R3.

[0042] Here, as an example of the alkoxy radical which has the hydrocarbon group of carbon numbers 1-20, a methoxy group, an ethoxy radical, a propoxy radical, a butoxy radical, etc. can be mentioned.

[0043] A propenyloxy radical etc. can be mentioned as an example of the alkenyloxy radical which has the hydrocarbon group of carbon numbers 1-20. A phenoxy group, a benzyloxy radical, etc. can be mentioned as an example of an aryloxy group.

[0044] Moreover, as an alkoxysilane compound used for this invention, the silane compound expressed with the following type (3) type can be used.

$$R4(SiOR5)2 \times R6 \dots (3)$$

However, in the above-mentioned formula (3), R4 is the radical expressed with R1 of said formula (2), and the same radical. R5 is the radical expressed with R1-R3 of said formula (2), and the same radical. R6 is the radical expressed with R3 of said formula (2), and the same radical, and x is two or more integers.

[0045] As an example of a compound expressed with the above-mentioned formula (2) or (3), the trialkyl oxy-vinylsilane which has the hydrocarbon group of carbon numbers 1-20, the dialkyl oxy-vinylsilane which has the alkyl group which has the hydrocarbon group of carbon numbers 1-20, the monoalkyl oxy-vinylsilane which has the hydrocarbon group of carbon numbers 1-20, a vinyl compound, and an acryloxy (meta) compound can be mentioned.

[0046] Here as a concrete example of the trialkyl oxy-vinylsilane which has the hydrocarbon group of carbon numbers 1-20 Vinyltrimethoxysilane, vinyltriethoxysilane, a vinyl tripropoxy silane, BINIRUTORI butoxysilane, a BINIRUTORI pentoxy silane, etc.; (meta) Acrylate trimethoxysilane, Acrylate triethoxysilane, an acrylate (meta) tripropoxy silane, (meta) Bitter taste relay TOTORI butoxysilane, an acrylate (meta) TORIPENTOKI gardenia fruit run, etc.; (meta) Acryloxyethyl trimethoxysilane, (Meta) Acryloxyethyl triethoxysilane, an acryloxyethyl (meta) tripropoxy silane, (Meta) (Meta) Acryloxy ECHIRUTORI butoxysilane (meta), Acryloxy ECHIRUTORI pentoxy silane etc.; (Meta) [Acryloxypropyltrimethoxysilane,] Acryloxypropyltriethoxysilane, an acryloxypropyl (meta) tripropoxy silane, (Meta) Acryloxy propyl RIRUTORI butoxysilane, an acryloxy (meta) PUROPRIUTORI pentoxy silane, etc.; (meta) Acryloxy methoxy propyltriethoxysilane, (Meta) Acryloxy methoxy propyl triethoxysilane, acryloxy (meta) methoxy PUROPRIUTORI propoxysilane, (Meta) Acryloxy methoxy PUROPRIUTORI butoxysilane, acryloxy (meta) methoxy propyl TORIPENTOKISHISHIRAN, etc.; (meta) Acryloxy ethoxy propyltriethoxysilane, (Meta) Acryloxy ethoxy propyl triethoxysilane, acryloxy (meta) ethoxy PUROPRIUTORI propoxysilane, (Meta) Acryloxy ethoxy PUROPRIUTORI butoxysilane, acryloxy (meta) ethoxy propyl TORIPENTOKISHISHIRAN, etc.; (meta) Acryloxy propoxy propyltriethoxysilane, (Meta) Acryloxy propoxy propyl triethoxysilane, acryloxy (meta) propoxy PUROPRIUTORI propoxysilane, (Meta) (Meta) Acryloxy propoxy PUROPRIUTORI butoxysilane, acryloxy (meta) propoxy propyl TORIPENTOKISHISHIRAN, etc. can be mentioned.

[0047] As an example of the dialkyl oxy-vinylsilane which has the hydrocarbon group of carbon numbers 1-20 Vinylmethyldimethoxysilane, vinylmethyldiethoxysilane, a vinyl methyl dipropoxy silane, Vinyl methyl dibutoxysilane, a vinyl MECHIRUJI pentoxy silane, etc.; Vinylmethoxyxysilane, Vinyl diethoxysilane, a vinyl dipropoxy silane, vinyl dibutoxysilane, BINIRUJI pentoxy silane etc.; (meta) Acrylate methyl dimethoxysilane, Acrylate methyldiethoxysilane, an acrylate (meta) methyl dipropoxy silane, (Meta) Acrylate methyl dibutoxysilane, an acrylate (meta) MECHIRUJI pentoxy silane, etc.; (meta) Acrylate dimethoxysilane, (Meta) Acrylate diethoxysilane, an acrylate (meta) dipropoxy silane, (Meta) Acrylate dibutoxysilane, (Meta) Acrylate diethoxysilane, an acrylate (meta) dipropoxy silane, etc.; (meta) Acrylate dimethoxysilane, (Meta) Acrylate diethoxysilane, an acrylate (meta) JIPENTOKI gardenia fruit run, etc.; (meta) Acrylate dimethoxysilane chloride, (Meta) (Meta) Acrylate diethoxysilane chloride (meta), acrylate dipropoxy silane chloride, (Meta) Acrylate dibutoxysilane chloride (meta) Acrylate JIPENTOKISHI silane chloride etc.; (meta) [Acryloxyethyl dimethoxysilane,]

[illegible]

dibutoxysilane chloride, acryloxylethyl (meta) JIPENTOKISHI silane chloride, etc.; (meta) Acryloxypropyl dimethoxysilane, (Meta) Acryloxypropyl diethoxysilane, an acryloxypropyl (meta) dipropoxy silane, (Meta) Acryloxypropyl dibutoxysilane, an acryloxy (meta) PUOPIRUJI pentoxy silane, etc.; (meta) Acryloxy methoxy propyl dimethoxysilane, (Meta) Acryloxy methoxy propyl diethoxysilane, acryloxy (meta) methoxy PUOPIRUJI propoxysilane, (Meta) Acryloxy methoxy propyl dibutoxysilane, acryloxy (meta) methoxy propyl JIPENTOKISHISHIRAN, etc.; (meta) Acryloxy ethoxy propyl dimethoxysilane, (Meta) Acryloxy ethoxy propyl diethoxysilane, acryloxy (meta) ethoxy PUOPIRUJI propoxysilane, (Meta) Acryloxy ethoxy propyl dibutoxysilane, acryloxy (meta) ethoxy propyl JIPENTOKISHISHIRAN, etc.; (meta) Acryloxy propoxy propyl dimethoxysilane, (Meta) Acryloxy propoxy propyl diethoxysilane, acryloxy propoxy PUOPIRUJI propoxysilane, (Meta) Acryloxy propoxy propyl dibutoxysilane, acryloxy (meta) propoxy propyl JIPENTOKISHISHIRAN, etc.; A vinyl methoxymethyl silane, (Meta) A vinyl ethoxymethyl silane, vinyl propoxysilane, vinyl butoxy methylsilane, vinyl pentoxy methylsilane, etc. can be mentioned.

[0048] moreover, as an example of the monoalkyl oxy-vinylsilane which has the hydrocarbon group of carbon numbers 1-20 Vinyl methoxymethyl silane chloride, vinyl ethoxymethyl silane chloride, Vinyl propoxysilane chloride, vinyl butoxy methylsilane chloride, Vinyl pentoxy methylsilane chloride etc.; Vinyl methoxy dimethylsilane, Vinyl ethoxy dimethylsilane, vinyl propoxy dimethylsilane, Vinyl butoxy dimethylsilane, vinyl pentoxy dimethylsilane, etc.; (meta) Acrylate methoxy methylsilane, Acrylate ethoxy methylsilane, acrylate (meta) propoxy methylsilane, (Meta) Acrylate butoxy methylsilane, acrylate (meta) pentoxy methylsilane, etc.; (meta) Acrylate methoxy methylsilane chloride, (Meta) Acrylate ethoxy methylsilane chloride, acrylate (meta) propoxy methylsilane chloride, (Meta) Acrylate butoxy methylsilane chloride, acrylate (meta) pentoxy methylsilane chloride, etc.; (meta) Acrylate methoxy dimethylsilane, (Meta) Acrylate ethoxy dimethylsilane (meta), acrylate propoxy dimethylsilane, (Meta) Acrylate butoxy dimethylsilane, acrylate (meta) pentoxy dimethylsilane, etc.; (meta)-

[Acryloxyethyl methoxy methylsilane,] Acryloxyethyl ethoxy methylsilane, acryloxyethyl (meta) propoxy methylsilane, (Meta) Acryloxyethyl butoxy methylsilane, acryloxyethyl (meta) pentoxy methylsilane, etc.; (meta) Acryloxyethyl methoxy methylsilane chloride, (Meta) Acryloxyethyl ethoxy methylsilane chloride, acryloxyethyl (meta) propoxy methylsilane chloride, (Meta) Acryloxyethyl butoxy methylsilane chloride, acryloxyethyl (meta) pentoxy methylsilane chloride, etc.; (meta) Acryloxypropyl methoxy methylsilane, (Meta) Acryloxypropyl ethoxy methylsilane, acryloxypropyl (meta) propoxy methylsilane, etc.; (meta) Acryloxypropyl butoxy methylsilane chloride, (Meta) Acryloxypropyl methoxy methylsilane chloride, (Meta) Acryloxypropyl ethoxy methylsilane chloride, acryloxypropyl (meta) propoxy methylsilane chloride, (Meta) Acryloxypropyl butoxy methylsilane chloride, acryloxypropyl (meta) pentoxy methylsilane chloride, etc.; (meta) Acryloxypropyl methoxy dimethylsilane, (Meta) Acryloxypropyl ethoxy dimethylsilane, acryloxypropyl (meta) propoxy dimethylsilane, etc.; (meta) Acryloxy methoxy PUROPURMETOKISHI methylsilane, (Meta) Acryloxy methoxy PUOPURMETOKISHI methylsilane, acryloxy (meta) METOKISHIPUROPURU propoxy methylsilane, (Meta) Acryloxy methoxy PUOPURBUTOKISHI methylsilane, acryloxy (meta) METOKISHIPUOPURU butoxy methylsilane, etc.; (meta) Acryloxy METOKISHIPUOPURU propoxy methylsilane, acryloxy (meta) METOKISHIPUOPURU butoxy methylsilane, etc.; (meta) Acryloxy

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methoxy PUROPIRUBUTOKISHI dimethylsilane, acryloxy (meta) METOKISHIPUROPIRU pentoxy
dimethylsilane, etc.; (meta) Acryloxy ethoxy PUROPIRUMETOKISHI methylsilane, (Meta)
Acryloxy ethoxy PUROPIRUETOKISHI methylsilane, acryloxy (meta) ETOKISHIPUROPIRU
propoxy methylsilane, (Meta) Acryloxy ethoxy PUROPIRUBUTOKISHI methylsilane, acryloxy

temperature (meta) has good bond strength to the polyimide orientation film by heating

pressurization adhesion, its difference between the coefficient of thermal expansion of an acrylic (meta) adhesive property resin particle and the coefficient of thermal expansion of a pasted up object decreases, and exfoliation of the liquid crystal device by the difference of such a coefficient of thermal expansion stops being able to generate it easily.

[0063] 1-20 micrometers of mean particle diameter of this (meta) acrylic adhesive property resin particle are usually within the limits of 3-15 micrometers preferably. As for the particle diameter of this acrylic adhesive property resin particle, having gathered as much as possible is desirable, and 15% or less of CV values which show dispersion in a particle is usually in 10% or less of within the limits preferably.

[0064] When mean particle diameter of the spacer particle used is made into 100% from this (meta) acrylic adhesive property resin particle being used with a spacer particle, the mean particle diameter of this (meta) acrylic adhesive property resin particle usually has the particle diameter of 130 - 170% of within the limits preferably 101 to 200%.

[0065] The acrylic (meta) adhesive property resin particle of this invention has elasticity, and it pastes up a substrate, being crushed in a cross-section ellipse form to the particle diameter of a spacer with the pressure in the case of heating sticking by pressure. Therefore, while an acrylic (meta) adhesive property particle is crushed in a cross-section ellipse form, a substrate and this particle carry out field contact by contacting a substrate. That is, if the particle diameter of an acrylic (meta) adhesive property resin particle is the same as the particle diameter of a spacer particle or the particle diameter of an acrylic (meta) adhesive property resin particle is small, since the distance between substrates will be regulated by the hard spacer particle, point contact of a substrate and the adhesive resin particle is carried out. For this reason, it is hard to discover adhesive strength firm between a substrate and an adhesive resin particle. On the other hand, by having elasticity like the acrylic (meta) adhesive property resin particle used by this invention, and moreover using a larger particle than a spacer particle, in the case of heating sticking by pressure, an acrylic (meta) adhesive property resin particle is ***(ed) between substrates, and it deforms to the particle diameter of a spacer particle. In this way, in connection with a particle deforming, ** becomes that the bond strength of a particle and a substrate does not have less, and the contact to a particle and a substrate can maintain high adhesive strength for a long period of time, when it changes to field contact from point contact and a touch area becomes large.

[0066] Such (meta) an acrylic adhesive property resin particle can be manufactured by carrying out the polymerization of the above monomer components using a reaction initiator. It is desirable especially to use churning means, such as a homogenizer, for the above-mentioned monomer component, a reaction initiator, and an emulsifier by this invention, to emulsify or distribute aqueous media, such as water, and to perform a polymerization. 40-150 degrees C of reaction temperature in this case are usually 60-120 degrees C preferably, and reaction time is usually 2 - 12 hours preferably for 1 to 24 hours.

[0067] Moreover, it is desirable to perform the above-mentioned reaction to the bottom of existence of a seed particle. Mean particle diameter is the particle which is usually within the limits of 0.3-20 micrometers, and the seed particle used here is a particle which usually has preferably 10% or less of CV values to 5% or less. By making it distribute in an aqueous medium and carrying out the polymerization of the above-mentioned monomer component to the bottom of coexistence of this particle, it reacts, while a monomer component is incorporated by the seed particle, and a seed particle grows.

[0068] As a seed particle used here, it is desirable that it is an acrylic (meta) (**) polymer particle, and this (meta) acrylic (**) polymer particle can be manufactured, when micro-disperse of the above-mentioned acrylic (meta) monomer is carried out and it carries out a polymerization into an aqueous medium.

[0069] such a seed particle -- the monomer component 100 weight section -- receiving -- usually -- the 1 - 100 weight section -- it is preferably used in the amount of 3 - 50 weight section. In this way, the obtained reactant can also be used with a reaction solvent, and separates a particle from the aqueous medium which is a reaction solvent, and it is used, refining it as occasion demands.

[0070] Furthermore, the particle separated in this way can also be dried and used, and it can also be used for it, being able to distribute still more nearly another dispersion-medium object anew. Next, the spacer constituent of the liquid crystal device concerning this invention is explained.

[0071] The spacer constituent of the liquid crystal device of this invention consists of a spacer and the aforementioned (meta) acrylic adhesive property resin particle. The spacer particle used for this invention is chosen from the group which consists of an organic polymer particle, an inorganic particle, and a composite particle.

[0072] As an example of an organic polymer particle, among such spacer particles A polyethylene particle, a polypropylene particle, the poly methyl pentene particle, A polyvinyl chloride particle, the poly tetrapod full ORAIDO particle, the poly divinylbenzene particle, A polystyrene bridge formation particle, a polystyrene isoprene bridge formation particle, a polymethylmethacrylate bridge formation particle, A vinyl polymer particle like the poly acrylic bridge formation particle; A polyethylene terephthalate particle, A polybutylene terephthalate particle, a polyamide particle, a polyimide particle, A polysulfone particle, a polyphenylene oxide particle, a polyacetal particle. An organic polymer particle like a benzoguanamine formaldehyde polymer particle; condensation particle [of an organic silane compound like tetra-alkoxysilane and trialkoxysilane]; etc. can be mentioned.

[0073] Moreover, as an inorganic particle, an inorganic oxide particle, an inorganic carbide particle, and an inorganic nitride particle can be mentioned. More specifically, a silica particle, an alumina particle, a glass particle, the condensation particle of tetra-alkoxysilane and a metal alkoxide, etc. can be mentioned.

[0074] 0.1-100 micrometers of 0.5-20 micrometers of usual of the average diameter of such a spacer particle are 1-10 micrometers still more preferably preferably. In addition, although it is the organic polymer particle spherical as a spacer and the spherical inorganic particle which are preferably used by this invention, even if these spacers are spherical, you may have configurations except spherical, such as the shape of fibrous, cylindrical, and an ellipse ball.

[0075] The spacer constituent of the liquid crystal device of this invention is obtained by mixing ** in such a spacer and the above (meta) acrylic adhesive property resin particles; the acrylic (meta) adhesive property resin particle mentioned above to said spacer 100 weight section in the spacer constituent of the liquid crystal device concerning this invention -- usually -- the 10 - 10000 weight section -- desirable -- the 50 - 5000 weight section -- it is used in the amount of the 100 - 1000 weight section within the limits still more preferably.

[0076] (Meta) Into the medium which does not dissolve or swell these components, homogeneity distributes and an acrylic adhesive property resin particle and a spacer can be applied as a constituent for spacers. As a medium, although an organic solvent can also be used, since the acrylic (meta) adhesive property resin particle of this invention is manufactured by carrying out the polymerization of the monomer component in an aqueous medium, into such an aqueous medium, it can distribute a spacer particle and can also consider as the constituent for spacers here.

[0077] The spacer constituent of the liquid crystal device of this invention is preferably used for a liquid crystal device as shown in drawing 1. The example of liquid crystal device structure is shown in drawing 1. In the substrate of a pair with which the orientation film C and C was formed on the transparency substrates A and A with which the electric conduction film B and B was formed, as for a liquid crystal device which is illustrated by drawing 1, a substrate is arranged at abbreviation parallel so that this orientation film may counter. Thus, between the substrates of the arranged pair, the acrylic (meta) adhesive property resin particle 1 is mostly distributed by homogeneity, and the uniform gap is formed between the substrates of a pair. The gap for liquid crystal restoration formed between substrates is usually 0.5-20 micrometers almost in accordance with the particle diameter of the spacer particle 2.

[0078] There is an acrylic (meta) adhesive property resin particle crushed in the cross-section ellipse form in the gap regulated by the spacer particle at drawing 1, and the condition that the orientation film pasted up mutually by this (meta) acrylic adhesive property resin particle is shown.

[0079] And huge gelation of the alkoxy group in the component unit guided from the glycidyl group or alkoxy silane in the component unit guided from the glycidyl (meta) acrylate which exists in an acrylic (meta) adhesive property resin particle is carried out according to self-bridge formation with heating by carrying out heating sticking by pressure. Therefore, since the polymer of low molecular weight hardly exists in the acrylic (meta) adhesive property resin particle after carrying out heating sticking by pressure, it is stable to liquid crystal. For this reason, even if it fills up with liquid crystal the gap formed using the constituent for spacers of this invention, liquid crystal is not influenced by the acrylic (meta) adhesive property resin particle.

[0080] Moreover, it does in this way, and the acrylic (meta) adhesive property resin particle (particle which is deforming into the ellipse form) after carrying out heating sticking by pressure is acrylic (meta) adhesive property resin particle itself that deformed functions as a spacer. Furthermore, when an acrylic (meta) adhesive property resin particle changes to a spacer expansively by heating sticking by pressure in this way, migration of the spacer particle blended from the beginning is prevented by the newly formed spacer. Therefore, migration of the spacer particle in liquid crystal can be prevented effectively.

[0081] Thus, since it is lost that a spacer is unevenly distributed by using the spacer constituent of this invention, an extremely stable large-sized liquid crystal device can be manufactured by using the constituent for spacers of this invention.

[0082]

[Effect of the Invention] Since the adhesive resin particle for spacers concerning this invention becomes acrylic adhesive property resin from the acrylic (meta) adhesive property resin particle which glycidyl (meta) acrylate 10 - 60 weight sections, and/or the alkoxy silane compound 1 - 10 weight sections copolymerized as described above (meta), it excels in an adhesive property, and it excels in the adhesive property with the orientation film which constitutes especially a liquid crystal device. Moreover, since the adhesive resin particle for spacers concerning this invention does not contain a curing agent, it does not have a possibility that the display function of liquid crystal may fall, either, and it is excellent also in adhesive strength with a substrate. Moreover, since the spacer constituent of the liquid crystal device concerning this invention consists of the above mentioned adhesive resin particle for spacers and the above mentioned spacer particle, it fits especially manufacture of a large-sized liquid crystal device.

[0083]

[Example] Although this invention is explained still more concretely below based on an example, this invention is not restrictively interpreted according to the following examples.

[0084] [The Measuring condition of physical properties]

With the measurement scanning electron microscope of the CV value of mean particle diameter and particle size, the particle size of 200 particles is measured and mean particle diameter and a CV value are calculated.

[0085] 0.1g of adhesion test particles was applied for 5 minutes to the bottom of the exposure of a supersonic wave, and 20g (a mixed capacity factor = 1:1) of water-isopropyl alcohol (IPA) mixed solutions was made to distribute them. These dispersion liquid were sprinkled on the polyimide orientation film of a glass substrate with the polyimide orientation film (40mm×45mm), and were dried under 60 degrees C for 1 hour. Heating adhesion of this substrate was carried out by the pressure of 50 g/cm², 100 g/cm², 200 g/cm², 400 g/cm² under 150 degrees C for 1 hour, and the sample substrate was prepared. Bond strength was measured with the tension tester using this prepared sample substrate.

[0086]

[Example 1] Emulsification micro-disperse of the solution obtained by dissolving benzoyl peroxide (BPO) 1g in mixed liquor (methyl methacrylate 25g, isobutyl methacrylate 30g, and glycidyl methacrylate 40g) was carried out to 160g of water.

[0087] Thus, the PMMA particle (mean particle diameter of 2.9 micrometers, 3% of CV values) which is a seed particle supplied 15g of water dispersions to the prepared emulsification dispersion liquid A in 30% of the weight of the amount, and it warmed at 40 degrees C, and agitated for 1 hour.

[0088] In this way, 40g of 5-% of the weight water solutions of polyvinyl alcohol (Kuraray make-VA-420) was added to the prepared dispersion liquid. After addition, these dispersion liquid were warmed at 75 degrees C, it maintained to this temperature for 3 hours, and the uniform real ball particle of the mean particle diameter of 8 micrometers and 7% of CV values was obtained.

[0089] 200ml of ion exchange water washed the obtained particle 3 times, it was dried 50 degrees C for 72 hours, crack classification was carried out and 70g of uniform real ball fine-particles particles of the mean particle diameter of 8 micrometers and 4.0% of CV values was obtained. The adhesion test was performed using the obtained particle.

[0090] A result is shown in Table 1.

[0091]

[Example 2] In the example 1, 70g of uniform real ball fine-particles particles of the mean particle diameter of 8 micrometers and 4.2% of CV values was obtained like the example 1 except having used isobutyl methacrylate 65g, having used 2g of gamma-methacryloxypropyl trimethoxy silane instead of glycidyl methacrylate 40g instead of methyl methacrylate 28g, and having prepared emulsification micro-disperse liquid B. The adhesion test was performed using the obtained particle.

[0092] A result is shown in Table 1.

[0093]

[Example 3] In the example 1, 70g of uniform real ball fine-particles particles of the mean particle diameter of 8 micrometers and 4.5% of CV values was obtained like the example 1 except having prepared the emulsification dispersion liquid C which used methyl methacrylate 23g, isobutyl methacrylate 30g, glycidyl methacrylate 40g, and 2g of methacrylic acids instead of methyl methacrylate 25g, isobutyl methacrylate 30g, and glycidyl methacrylate 40g. The above mentioned adhesion test was performed using the obtained particle.

[0094] A result is shown in Table 1.

[0095]

[Example 4] In the example 1, 70g of uniform real ball fine-particles particles of the mean particle diameter of 8 micrometers and 4.1% of CV values was obtained like the example 1 instead of methyl methacrylate 25g, isobutyl methacrylate 30g, and glycidyl methacrylate 40g except having prepared emulsification dispersion liquid D using methyl methacrylate 20g, isobutyl methacrylate 30g, glycidyl methacrylate 40g, and 2-hydroxyethyl methacrylate 5g. The above mentioned adhesion test was performed using the obtained particle.

[0096] A result is shown in Table 1.

[0097]

[The example 1 of a comparison] The presentation ratio (the weight (ratio i) / (ii)) of isobutyl methacrylate (i) and methyl methacrylate (ii) performed the above mentioned adhesion test using 90/10 of seed polymerization particles (mean particle diameter of 8 micrometers, 4.5% of CV values).

[0098] A result is shown in Table 1.

[0099]

[The example 2 of a comparison] The presentation ratio (weight (ratio i) / (ii)/(iii)) of isobutyl methacrylate (i), methyl methacrylate (ii), and ethylene glycol dimethacrylate (EGDMA) (iii) performed the above mentioned adhesion test using the seed polymerization particle (mean particle diameter of 8 micrometers, 4.2% of CV values) of 90/5/5.

[0100] A result is shown in Table 1.

[0101]

[Example 5] It used 10mg of 5-micrometer silica particles as 100mg of particles and the spacer particle of an example 1, and the above mentioned adhesion test was performed.

[0102] A result is shown in Table 1.

[0103]

[Table 1]

圧力条件 (g/cm^2)	検 査 強 度 (g/cm^2)				
	実施例 1	実施例 2	実施例 3	実施例 4	実施例 5
50	65	70	52	59	25
100	93	105	73	89	29
200	122	121	80	118	48
400	130	145	93	137	56

[Translation done]

* NOTICES *

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the schematic drawing showing the example of liquid crystal device structure typically.

[Description of Notations]

- 1 ... Adhesive resin particle for spacers
- 2 ... Spacer particle
- A ... Transparency substrate
- B ... Transparency electric conduction film
- C ... Orientation film

[Translation done.]